
Description

~~Fully-closed, zero-discharge~~ Fully-closed, zero-discharging, clean oxidizing pulping technology process and process the preparation thereof

Field of the invention

The invention relates to a clean, fully-closed, zero-discharging pulping process by oxidation and the preparation method thereof ~~for a fully-closed, zero discharge, clean oxidizing pulping technology and process. In particular, it is practically relates to a clean pulping process having the characteristics of that involves a method with~~ close-loop, self-cycling, ~~no~~ no acid used, ~~no~~ no alkali used, ~~no~~ no chlorine used, ~~no~~ no anthraquinone used-, ~~no~~ no cooking needed, ~~no~~ no bleaching needed, ~~no~~ no draining and ~~no~~ no pollution.

Background of the invention

Short supply of papermaking materials is a problem faced by the pulping & papermaking industry in a long term and occurs not in a single district but in ~~worldwide~~ the whole world. Forest acts as the lung of earth that can absorb carbon dioxide and produce oxygen in addition to the ~~effect~~ effects on the conservation of -water resources, prevention of soil erosion, and adjustment of climate. And it has both ecological and economic ~~value~~ values. However, it is now decreasing at a rate of $700 \times 10^8 \text{ m}^2$ yearly per year and tropical rain forest is ~~being reduced~~ decreasing at a rate of $50 \times 10^4 \text{ m}^2$ per minute. If the illegal ruinous exploitation is not strictly restricted, with the increasing of the whole world population, human beings may have to face the dilemma of ~~no~~ no adequate oxygen to breathe 40 years later.

According to a comparison of the China Forestry Statistical Yearbook in 1999 with the one in 2000 ~~compared with 1999~~, the decreasing rate of forest area ~~in~~

2000 is: ten major forestry ecological programs -12.9%, ~~natural~~ naturally formed forest conservation program -10.7%, area of ~~enclosure of~~ the hillside closed for regeneration of forest -6.33%, protection forest ~~+24.75%~~ -24.75%, economic plantations ~~-3.83~~ -3.82% and forest of for commercial timber -14.07%.

Based on the plant fiber—cellulose chemistry, non-wood fiber—cellulose materials can be categorized as: 1. ~~the~~—grass gramineous fiber materials; —2. ~~base~~ phloem fiber materials; 3. cotton linters fiber materials;— 4. leaf fiber materials. And the holocellulose content of non-wood fiber materials is 48%-84%. The length of most non-wood fiber is longer than that of wood fiber, ~~and cellulose~~ Cellulose is the main content material used in papermaking. Cellulose extracted either ~~both~~ from wood ~~and~~ or from non-wood materials can be used as supporting materials of paper and for the production of raw material materials of middle or high quality pulp. It is demonstrated that in the fiber of non-wood materials such as cotton stalk, all kinds of chemical components are similar to that of ~~hard~~—broad-leaved wood and ~~soft~~—needle-leaved wood.

China is an agricultural country and also ~~is~~ a cotton-producing country. ~~Annual~~—The yield of annual plant resource ~~that can compare favorably with wood~~ is about ~~0.16 billion~~ 160 million tons (t), which is comparable to the wood resource. During the “Ten-Five” plan Plan, the growing area in the major cotton-producing ~~area~~—regions of China is expected to be ~~is~~ stabilized at a level of 6 million hm² in 2010. There are 34.2 million tons of high quality cotton stalks annually. Based on the data ~~of~~ in textbook, output of cotton stalk pulp is 24.282 million tons. If the utilization ratio is 20%, the output is 4.856 million ~~t/y~~ tons/year, however, heretofore, the utilization ratio of the annual plant resource ~~resembled~~ resembling the ~~hard~~ broad-leaved wood is less than 1%. ~~0.235 billion~~ 235 million tons of non-wood fiber materials ~~of non-wood~~ can be extracted from cornstalk,

wheat straw, rice straw (in accordance with ~~year 2000~~ agriculture statistical yearbook Agriculture Statistical Yearbook of 2000, ~~the yield thereof of them~~ has already attained ~~reached~~ 0.47 billion 470 million tons). Now utilization ratio of the vast pulping resource of annual plant ~~pulp materials~~ is less than 5%. These annual plant resources are called ~~agriculture~~ agricultural green waste in ~~America~~ the United States, and are called green annual plant resource in China.

In “Pulping Technology and Equipment” ~~that~~ published by China Light Industry Publishing House ~~in year 2000~~, the ~~content~~ contents of holocellulose of various fiber materials ~~tested~~ determined by ~~with sodium chlorite is~~ are disclosed, ~~listed as shown~~ in table 1.

Table 1 unit: weight %

Materials	Production Place	Holocel lulose	Materials	Production Place	Holocellulo se
spruce	xiaoxinganling	73. 0	Wheat straw	Hebei	71. 3
korean pine	daxinganling	69. 6	Sugarcane <u>residue</u>	Guawngdong <u>Guangdong</u>	75. 6
populus xiaozuanyangica	henan	81. 6	Chinese alpine rush	Guangxi	76. 7
bambusa oldhami	zhejiang	69. 5	Sorghum stalk	Hebei	66. 4
Bambusa eduldoides	Guangdong	67. 2	Corn stalk	Hebei	84. 9
phragmites communis	Hubei	75. 4	Achnatherum	Jingxia <u>Ningxia</u>	79. 8
gossypium hirsutum	Jiangsu	75. 1	Deyounia angstyolia	Heilongjiang	74. 9
<u>cotton stalk</u>			Chinese silvergrass	Sichuan	84. 3
rice strew <u>straw</u>	Hebei	64. 0			

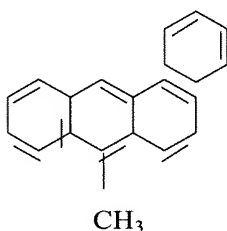
In “Plant Fiber Cellulose Chemistry” that published by China Light Industry Publishing House ~~in year 2001~~, data ~~of~~ for chemical analysis of cotton stalk

materials chemical analysis (weight%) and average staple length of fibers (mm) is are listed in table 2.

Table 2

Part of cotton stalk	moisture	ash	extractive extract				Sodium chlorite holocellulose	Klason Lignin	Poly pentose	Pectin	Average fiber
			Cold water	Hot water	1% NaOH	Phenyl alcohol					
Cotton stalk peel	6.12	6.12	18.34	23.66	43.57	2.7	75.57	16.84	23.26	9.64	2.46
Cotton cane	7.87	2.05	3.71	5.02	21.36	1.68	76.32	21.31	18.07	1.42	1.08
Full cotton stalk	8.12	3.15	7.68	9.74	28.72	1.94	75.95	20.17	19.27	4.25	1.68

It is well-known that ~~worldwide~~ worldwide papermaking worldwide still uses the traditional process invented before 100 years in which strong acid acids, strong alkali alkalis, strong chlorine are used and black liquor is drained without restraint. The traditional process has seriously impacted the environment that humankind human beings ~~relies~~ rely on for ~~existence~~ living. In recent years Anthraquinone ~~anthraquinone~~ is introduced in papermaking of ~~in~~ Japan, India, Canada etc. Anthraquinone belongs to the is a fused polycyclic aromatic hydrocarbon ~~hydrocardes~~ of arenes. All of the ~~The~~ fused polycyclic aromatic hydrocarbons ~~hydrocardes~~ have been confirmed to be the ~~carcinogen~~ carcinogenic. For instance, a known carcinogen structure made of anthracene is as follows:



10-Methyl-1,2-benzanthracene ~~(ethene)~~ or ethylene-1, 2-benzanthracene

The ~~prohibition order relating to the prohibition of chlorine in~~ of pulp bleaching with chemicals relate to chlorine was promulgated by Environmental Protection Agency (USA) in April 2000. More recently, 54% of papermaking companies paper mills in the world are fixing their eyes on ClO_2 as the bleaching agent. ~~Nevertheless, 91% of~~ ClO_2 may produce dioxine and other organic compounds, nevertheless, and the remained remaining 9% Cl_2 is discharged as ~~Cl_2 to the atmosphere,~~ which does harm the environment that human beings rely on.

The oxidizing bleaching of pulp can date back to the early 1950's. Oxygen was first found ~~that it has to have a~~ bleaching ability by Soviet wood chemist Nikieih—Nikieih and Arim ARim in 1952. Twelve years later, Magnesium ~~magnesium~~ salts are found to be able to avoid cellulose ~~oxidation~~ to be oxidized and ~~degradation~~ degraded by French scientist Rebeve et al in 1964. Laboratories ~~one after another~~ were established one after another in three countries (America U.S., France and Sweden) in 1970. In the same year, the first chlorine dioxide bleaching plant of the world was constructed in Enstrd of South Africa. In 1972, ClO_2 oxygen bleaching plant with a capacity of 12t/d was set up in ~~America—the~~ U.S. and the technology was patented. ~~But, however,~~ it was not industrialized put into service due to the great loss of cellulose, high energy consumption, and high water consumption and high production cost. Twenty-seven years later, Gerogelude Company in France (1999) and Prinsell Company in America (2001) successively used the combination of ClO_2 and O_3 for bleaching. But chlorine pollution was not ~~shaken off~~ gotten rid of. Referring to the patent patents before March, 2002 of all over the world, the ~~worldwide papermaking~~ worldwide stand still employed as the seriously polluting cooking process with strong acid, strong alkali and strong chlorine, and ~~stand still as~~ utilized the seriously polluting

bleaching process with chlorine. Treatment of lignin chromophores ~~chromophore~~ ~~stands still as~~ relied on the traditional process of separation and degradation of lignin used in 100 years before ago. For this reason, papermaking ~~of in~~ the world has become the ~~emphases~~ an important object of concern for the environment protection organization.

Pulp bleaching with ClO_2 and O_3 (CN1212310A) invented by France ~~liquid air company~~ Liquid Air Company was ~~made public~~ published on at March 31, 1999. Pulping ~~of~~ process using cornstalk and other non-wood fiber materials (CN1371439A) invented by ~~America~~ North Carolina State University of U.S. was ~~made public at~~ published on Sep 25, 2002. Other patent applications include: A method that produces pulp by a pulping process using non-wood material and its preparation system—equipment (CN1407172A) invented by Japan ~~business corporation~~ Business Corporation published on April 2, 2003, a pollution-free pulping method (CN1198492) invented by Shandong Weichang Normal University, a pulping method without alkali (CN1229155) and a pulp bleaching electrochemical technology of polyoxometallate (CN1458075) ~~were made public at April 2, 2003~~ et cetera.

Referring to all above ~~instruction~~ patents, some are related to bleaching method without chlorine, some aim at ~~are~~ reducing the ~~dosage~~ amount of acid, alkali and chlorine used, some are using ozone instead of chlorine, some are using alkali, anthraquinone and peroxide acid. Until March, 2002, there ~~are is~~ no ~~any plant~~ method which can finish degradation of lignin without using acid, alkali, and ~~no any plant puts down~~ method which eliminates the use of acid, alkali and chlorine completely, which implies that ~~illustrate~~ the pollution problem has not been ~~thoroughly~~ resolved in these patents. The present ~~patent~~ invention solves the pollution problem ~~of in~~ papermaking ~~thoroughly~~. The invention ~~gets rid of~~

solves the problem of using strong acid, strong alkali, chloride and anthraquinone ~~in pulping process~~, during the whole process of degradation of lignin and bleaching. All wastewater produced by papermaking ~~isn't~~ is not drained outwards. ~~The invention is~~, thereby forms a fully-closed, self-circling and ~~zero-discharge process~~ zero-discharging system, and completely solves two worldwide problems - materials material shortage of ~~pulping & papermaking~~ and serious pollution existing in pulping & papermaking industry.

Detailed description Summary of the invention

The invention overcomes the ~~current~~ technical shortcomings in the prior arts and provides a close-loop, self-cycling, ~~zero-discharge~~ zero-discharging, clean oxidizing pulping ~~technology~~ process and ~~process~~ the preparation method thereof.

~~Clean~~ The clean pulping process and preparation method thereof of the invention are ~~carried out by undermentioned technical projects~~ characterized in that. ~~The character of the invention is that~~ the raw materials of the clean pulping process and the preparation method thereof are non-wood ~~and or~~ wood material. ~~Preparation~~ preparation of the pulp can be finished according to undermentioned the ~~processes~~ mentioned below:

(A) Pretreatment of raw materials-;

(B) ~~Above materials~~ Materials pretreated above are oxidizing dipped ~~in water~~ in the presence of ~~that contains~~ active oxygen A and cellulose ~~preserver~~ that is made of protectant consisting of metal ions and metal ion ligands-;

(C) The ~~oxidizing-dipped~~ oxidizing materials are ~~grinded in turn~~ ground sequentially by the active oxygen A and then active oxygen B-;

(D) ~~Concentrate~~ Concentrating and beating-;

In accordance with the present invention, wherein, the active oxygen A is one or two selected from O_2 , H_2O_2 , and ~~one or two~~ free radicals generated from O_2 , ~~or~~ H_2O_2 ; The the active oxygen B is one or more selected from O_3 , 1O_2 (singlet oxygen), $O_2^{\cdot-}/HOO\cdot$ (superoxide anion radical), and ~~one or~~ multiform free radicals generated from O_3 , 1O_2 , $O_2^{\cdot-}/HOO\cdot$ therefrom in water in the presence of an ~~water in which organic solvent exists~~.

In accordance with the present invention, the organic solvent is, for example, is DMSO or oxalic acid acids.

A ~~kind of~~ pulp is obtained by the above process is also provided.

In ~~above the~~ clean pulping method described above, the non-wood materials such as full cotton stalk ~~includes~~ include one or the mixture of two or more selected from cellulose, hemicellulose, lignin of cotton bast, cotton stem, cotton stalk root and full cotton holocellulose, cellulose and hemicellulose of ~~valvular cotton, cotton short linter, cotton dregs, and cotton seed, a kind of lignin, or two or multi-kinds of their compounds~~. The ~~described~~ Said wood fiber woods includes ~~soft woods and hard wood~~ broad-leaved wood and needle-leaved wood, such as white pine, Masson pine, longitudinal white pine, oregano pine David poplar, aspen wood, fast-growing poplar, birch and so on.

In accordance with the invention, the metal ions are one or the mixture of two or more selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Si^{2+} ~~and two or multi-kinds of their compounds~~. The ~~metallie~~ metal ion ligands are one or the mixture of two or more selected from include dimethyl dioxirane (DMD) DMD, diethylenetriamine pentaacetic acid (DTPA) DTPA, ethylenediaminetetraacetic acid (EDTA) EDTA, alkyl-sulfonic acid sodium sodium alkylsulfonate, and polyoxyethylene alkylether poly-oxyethyl-enabkylether and two or multi-kinds of

their compounds.

~~In accordance with the invention,~~ Amount dosage of the metal ions in weight is between 1-1000ppm.

~~In accordance with the invention, the~~ The oxidizing dipping treatment is carried out in an acidic condition whose having a pH is of between 1-4, preferably, ~~and the best pH is between 1.5-2.5.~~

~~In accordance with the invention, the~~ The grinding treatment is carried out in an acidic condition whose having a pH is of between 1-4, preferably, ~~and the best pH is between 2.5-3.8.~~

~~In accordance with the invention, the~~ The acidic condition can be obtained by use of the active oxygen of the invention (such as $\text{HOO} \cdot$) and ~~also can~~ also be obtained by the addition of pH regulator.

~~In accordance with the invention, the~~ The concentration of active oxygen A in ~~above the~~ materials being treated is 0.01-2.0wt%, and the concentration of active oxygen B in above materials is 0.1-50umol/L.

A kind of clean pulping method as stated above has undermentioned characters the following features and advantages: (A) The active oxygen is dropped into the a disc refiner, in which heat energy is generated ~~through~~ from the rotation of the disc, and is ~~the energy is~~ transferred into the materials for reaction, thus ~~then~~ the fiber cellulose is separated from the intercellular space; (B) With ~~cooperation~~ the combined effects of the active oxygen A and B, the chromophoric ~~group~~ groups (α , β -aldehyde or ketone ~~group~~ groups) in the lignin is are transformed into ~~non-color group~~ less colorless groups (the i.e., carboxylic acid acids or binary acid carboxylic acids); (C) Self-cycling: the raw materials pre-treated are delivered to the oxidation reactor. All water used in the process

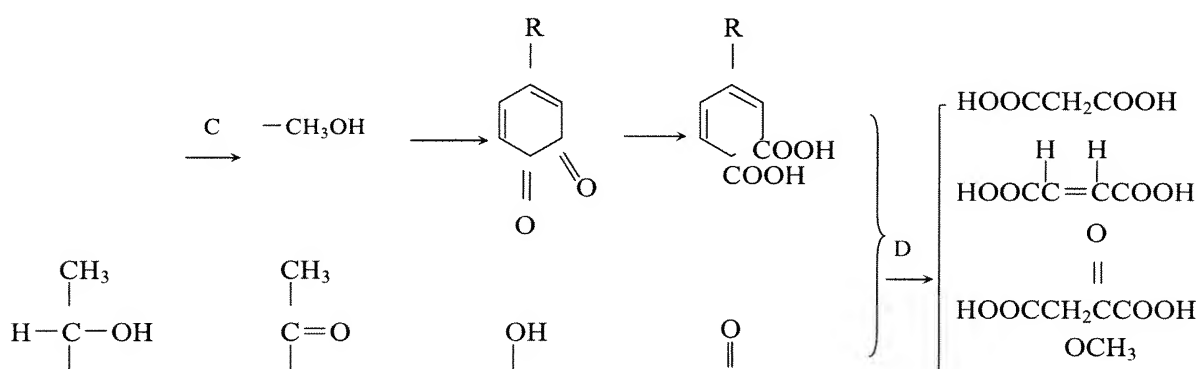
from the pretreatment of raw materials till the delivery of it to the oxidation reactor is divided into two parts to be to accomplish the self-cycling cycled in the process:- One the first part is the water from the ~~process of materials cleaning~~ pretreatment treatment of raw materials; after the centrifugal cleaning treatment, the resulting. It is purified by centrifugal cleaning and the solid sediments in it are taken away and the resulting. The pulps are sent to the ~~common~~ conventional beating process:- ~~Water~~ water generated in the process is ~~cycled~~ directed into a purification pool for cycling water in which —a 0.1%-0.15% ozonizer (O_3 generator) and acticarbon nutsch filter are is installed in the purification pool to decolor the water. The resulting water contains a very small amount of oxygen free radical and it is then pumped into the cycling water system; the ~~The other~~ second part is the water from the oxidizing process:- After which water is cleaned with ~~centrifugal cleaner~~ centrifugation and then is then concentrated with a common conventional decker, the The pulp is sent to the pulp tank and then to a for papermaking plant, and the The produced water produced is filtrated and then sent to placed in the water-purifying tank for self-cycling. The purified water is pumped into the materials cleaning system, ~~oxygen oxidizing~~ dipping system, oxygen grinding system and ~~filtrating~~ screening system for recycling use being recycled within the company.

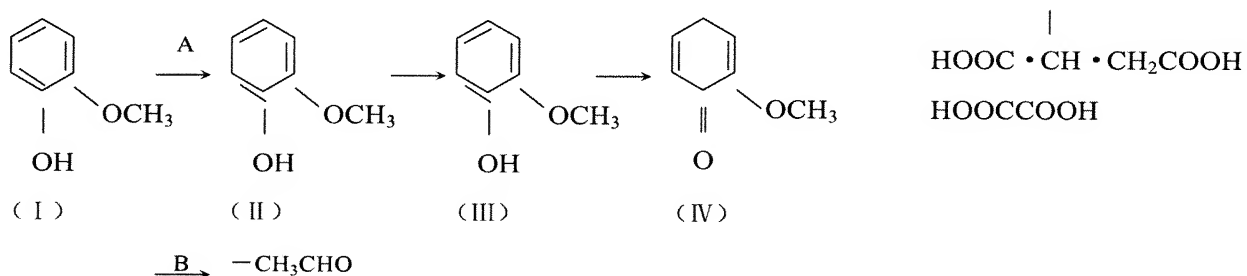
~~In accordance with the present invention, it takes advantage of~~ The present method employs active oxygen free radicals generated by ~~oxidation~~ electron-reduction reaction of molecular oxygen in an ion reactor to transform and separate lignin, ~~and to change chromophoric group groups~~ in the intercellular space and to obtain paper pulp. The conventional pulping technologies that use harmful polluting chemicals such as acid, alkaline, chlorine, anthraquinone and so on are basically ~~changed~~ different with the method of in

the present invention. ~~The~~ In the present invention, the cooking and bleaching process which, ~~generating~~ generate severe pollution, can be avoided. ~~The~~ , and the abundant ~~yearly~~ annually grown fiber materials can be utilized in this process and water and energy can be saved. As a result, the cost of production can be saved reduced.

~~In accordance with the invention, the~~ The active oxygen is added in into the materials, and ground with a high-concentration defibrator generates which leads to a grinding heat reaction by grinding, ~~which is used so as~~ to change lignin's ~~chromophore~~ chromophores of in the intercellular space. Because the hydroxyl ~~special~~ free radicals formed by the three oxygen atoms of ~~molecule~~ molecular oxygen has have a strong attack power and ~~internal~~ an intracellular nucleophilic attack power, ~~the~~ and an electrophilic reaction occurs between ~~special~~ the hydroxyl free radicals and lignin. The big π -bonds in the lignin structural ~~element~~ elements, i.e, benzene ring and ~~phenyl and exocyclic side chains~~, big π -bond are broken, and then lignin is ~~degraded~~ degraded and dissolved. The ~~chromophore~~ chromophores of in lignin is are changed transformed or decomposed into ~~low-molecular~~ small molecules, then ~~forms~~ achromic tintless ~~monocarboxylic acid~~ thus forming colorless monocarboxylic acids or binary carboxylic acid acids.

The reactions ~~Equations~~ are as follows:





The invention also includes the pulp made by the above process.

Process of the invention is described in detail-concretely as follows:

A clean oxidizing pulping process and the preparation method thereof,
~~characterized in that the~~ The character of the invention is that raw materials of
~~thereof the cleaning pulping process and the preparation method are~~ is
 non-wood and wood materials and . ~~Preparation preparation~~ of the pulp can be
 finished according to ~~undermentioned processes.~~ the following process:

(A) Pretreatment of raw materials:-_i

(B) ~~Above materials is~~ Materials pretreated above are oxidizing dipped in the
presence of ~~in the~~ active oxygen A and a cellulose preserver protectant that is
 made of metal ions and metal ion ligands:-_i

(C) ~~The oxidizing-dipped-oxidizing materials is grinded~~ are ground in turn by
 the active oxygen A and then active oxygen B:-_i

(D) ~~Concentrate~~ Concentrating and beating:-_i

wherein ~~In accordance with the present invention,~~ the active oxygen A is one
or two selected from O_2 , H_2O_2 , and ~~one or two~~ free radicals generated from O_2 ,
 H_2O_2 :-_i The the active oxygen B is one or more selected from O_3 , 1O_2 (singlet
 oxygen) $O_2^- / HOO \cdot$ $O_2^{\cdot-} / HOO \cdot$ (superoxide anion free radical) and ~~one or~~

multi-free radicals generated from therefrom $\text{O}_3, {}^1\text{O}_2, \text{O}_2^{\cdot-}/\text{HOO}\cdot$ in water in the presence of which an organic solvent exists.

Active oxygen can be obtained when molecular O_2 passes through an ion process radiator in which the an oxidation-reduction reaction can occur and the when energy is provided, and at last water is formed. In the process that four electrons are accepted, one oxygen free radical will be generated when one electron is absorbed by O_2 . For instance: hyperoxidized a hyperoxide anion free radical is formed when O_2 is reduced by one electron and its equation is: $\text{O}_2 + e \rightarrow \text{O}_2^{\cdot-}/\text{HOO}\cdot$. Hydrogen hydrogen peroxide is formed when O_2 is reduced by two electrons and its equation is: $\text{O}_2 + 2e + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$. Hydroxy hydroxy free radical is radicals are formed when O_2 is reduced by three electrons and free radical is radicals are formed by reaction of Fe^{2+} and H_2O_2 , which are special free radicals of for water treatment and their equations are: $\text{O}_2 + 3e + 3\text{H}^+ \rightarrow \text{H}_2\text{O} + \cdot\text{OH}$, $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$.

~~In accordance with the invention, the~~ The metal ions are ion(s) is/are one or the mixture of two or more selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , and Si^{2+} ~~and two or multi-kinds of their compounds and~~, the The metal ions are usually provided in the form of salt salts such as FeSO_4 , MgCO_3 , etc. The metallic metal ion ligands is ligand(s) is/are one or the mixture of two or more selected from for example DMD, DTPA, EDTA, alkyl-sulfonic acid sodium, poly-oxyethyl-enabkylether and two or multi-kinds of their compounds sodium alkyl-sulfonic acid, polyoxyethylene alkylether. Together with the The metal ion, the metallic metal ion ligand, hyperoxidized hyperoxide anion free radical ($\text{O}_2^{\cdot-}/\text{HOO}\cdot$ $\text{O}_2^{\cdot-}/\text{HOO}\cdot$) and H_2O_2 , they are combined together in different compositions to form a functional cellulose protection system systems which can

not only protect cellulose but also get rid of silicon.

Pretreatment usually includes removing impurity, ~~shear~~ shearing, fiberization fiberizing and, optionally, cleanout with concrete condition cleaning.

~~In accordance with the invention, the~~ The oxidizing-dipping treatment is preferably carried out in acidic condition ~~whose~~ wherein pH is between 1-4, and preferably, the best pH is between 1.5-2.5.

~~In accordance with the invention, the~~ The grinding treatment is carried out in acidic condition ~~whose~~ wherein pH for example is between 1-4, and preferably, the best pH is between 2.5-3.8.

~~In accordance with the invention, the~~ The acidic condition can be obtained by the use of active oxygen of the invention (such as $\text{HOO} \cdot$) and also can be obtained by the addition of a pH regulator.

The metal ions are usually used in the form of a salt and ~~its dosage range~~ the amount thereof is commonly between 1-1000ppm, preferably, ~~the best range~~ is between 10-100ppm—according to by weight of metal ion.

In accordance with the present invention, ~~the “non-cooking” involves~~ means that: the conventional cooking process can be omitted; instead, ~~The~~ the active oxygen is dropped into the disc refiner, in which heat energy is generated through the rotation of the disc, and ~~the~~ an energy ~~transferred~~ transferring reaction ~~is-generated~~ occurs, then the fiber cellulose is separated from the intercellular space.

In accordance with the present invention, ~~non-conventional~~ no conventional bleaching process needed ~~involves~~ means that: the bleaching process can be omitted—; instead, ~~The cooperation~~ the combined effects of the active oxygen A and B are used in order to transform the chromophoric ~~group~~ groups in the lignin

into ~~non-color group~~ colorless groups, ~~For~~ for example, to transform α , β -aldehyde or ketone ~~group-groups~~ are turned to the into carboxylic acid acids or binary acid acids.

In accordance with a preferred embodiment of the invention, ~~the detailed description of the process in the preferred implemented program is illustrated as follows~~ the process of the invention comprises:

The a pretreatment system ~~of~~ for the raw materials: This this is a cooperation process. In this process, legumen and calyces of the raw materials are removed ~~legumen, calyces~~ by a crushing engine, and then the raw materials are cut into pieces having a length of 5cm and thick ~~a thickness of 1.5cm and a yield of 98%,~~ Finally materials whose forming rate is 98% are obtained. Above materials are broken into plush plushes by roller and a rolling-type crushing engine, and then had removed dust and medulla removed by wind power while, ~~had~~ removed impurity removed by a cleaner; wherein, water used ~~Water of in~~ the cleaner is the water being cycled and full closed and ~~circular water in the factory, containing minor.~~ Little active oxygen free radicals and minor little cellulose preserver protectant (~~(could be brought commercially available)~~ from market) ~~are left in the water, so no~~ active oxygen needn't is needed to be added in the pretreatment process. No ~~any~~ drainage is drained discharged in the process of washing materials by circular the cycling water, which ~~changes~~ is different with the traditional ~~process with~~ acid washing and alkali washing process.

Oxidation reactor system (~~refer referring~~ to the application of patent for invention of China Chinese patent application No.: 200310103895.3): The the main function thereof is imbibition, softening and debonding of the materials; pH within the reactor is 1-4; Active active oxygen in the subacidity weak acidic water

whose pH is 1 to 4 generates superoxide anion radicals ($O_2^{\cdot -}/HOO \cdot$) which have strong penetrability and can penetrate intercellular space directly to induce an oxidation-reduction reaction. An agitator is installed in the oxidation reactor and the agitator connects outer power plant motor through the top of the reactor;

The agitator is equipped with at least three layers of propellers at least has three process propellers, and its rotating speed can be controlled. Start the agitator and then in the reactor, positive ions are produced in the water by the electrodes. Materials are softened by the combined effects cooperation of positive ions, pressure, temperature and shearing stress of the agitator. In the oxidation reactor, owing to the active oxygen, catenating layer, pectin, and poly pentose are decomposed at the same time, and decoloring reactions are occurred by high speed agitating of active oxygen occur during the high speed agitation.

With the repeatedly repeated experiments, the best-preferred reaction conditions are identified: pH in the reactor is 1.5-2.5 and a rotating speed of 40-80 r/s for 40-60min r/min and 0.02-0.1% cellulose preserver protectant that has been prepared is also added. In 40-60 minutes, in the reactor, chromophore of material changes chromophores in the raw materials change from deep yellow to pale white, then materials are washed repeatedly and squeezed for removing the water out.

Grinding system: the best-choice preferred is disk grinder system that is consists made of two parts, one is model RL50S disc refiner or high consistency defibrator and the other is oxidation reactor. The process has includes first refining and second refining. Active oxygen A is used in the first refining and

active oxygen B is used in the second refining. The raw materials exported by ~~from oxidation-oxidizing-dipping~~ system are fed to the refiner by a screw feeder continuously and equally homogeneously, then the materials are dipped by O₃ whose concentration is 1-15umol/L, weight percentage concentration of water is 30%, and pH is 2.5. Grinding rotating speed is 600-1200 ~~r/s~~ r/min and the gap between the disks is 0.2-0.15mm. In first refining, active oxygen A whose weight percentage concentration is 0.1-1.5 is added in the shower water to mix and grind with materials. The materials are softened ~~with~~ by grinding, and then the ~~cellulose~~ cellulose cladded in the intercellular space is separated. Main function of the grinding thermal reaction is ~~producing~~ to produce heat transfer reaction with confriction of refiner by ~~mix~~ mixing and grinding of active oxygen and material materials. Chromophore Chromophores of phenylpropane hydrocinnamic-alkyl is are oxidized by superoxide anion free radicals, molecular dioxygen oxygen and hydrogen peroxide. With softening temperature difference of differences among lignin, hemicellulose and cellulose, hydrophilic groups gotten ~~produced~~ from oxidized exiguous fibers can connect fundamental-chain be connected to the backbone of cellulose; as a result, yield is augmented ~~to~~ by 8-12%. Key of the invention is ~~condition~~ the conditions of the process (~~the detail instruction of the process~~ such as sequence, pH, temperature, dosage amount of active oxygen used, time, rotating speed, pressure and pulp concentration etc of the process as detailed in the present invention).

The process ~~has~~ includes a first refining and a second refining. ~~slag~~ Slag sifted grinding can be grinded ground and screened repeatedly ~~after screening~~. After being transferred to the ~~In cleaner-disposal process~~, edible citric acid aqueous solution whose weight percentage concentration is 0.12 and hydroxylamine whose weight percentage concentration is 0.01 are added and

sprinkled to prevent dandy worm and oxidative stain. According to routine beating process, the pulp is beaten and the pulp thus obtained is the original material pulp with a yield of 76% and an ISO whiteness of 52-65°. The process described above can be applied in the village and township enterprises in the area with abundant raw materials. ~~And the~~ The coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

The raw ~~materials-pulps~~ are fed to the refiner continuously and equally by a screw feeder homogeneously and continuously. In the first refining process O_2 (weight percentage concentration is 0.1) and/or H_2O_2 (weight percentage concentration is 1.5) prepared in advance are added dropwise to the pulp in a ratio of $-1:0.12-0.15$ (according to weight ratio) and mixed with the pulp in refiner at $60-80^{\circ}C$, $pH2.5-3.8$ and 12-15% consistency. The rotating speed of ~~which the refiner is~~ 1300 r/s r/min and the gap between the disks is 0.15-0.1mm. The pulp whiteness can be $60-75^{\circ}$. In the ~~secondary~~ second refining process O_3 (concentration is 10umol/L) and/or superoxide anion radicals ($O_2^{\cdot-}/HOO\cdot$ $O_2^{\cdot-}/HOO\cdot$) (concentration is 10umol/L) and/or singlet oxygen (1O_2) (concentration is 10umol/L) are added and mixed with the pulp at $80-100^{\circ}C$, $pH2.5-3.8$, 12-15% pulp consistency and 0.3-0.6_Mpa. The rotating speed of refiner disc is 1300 r/s r/min and the gap between the disks is 0.15-0.1mm. After 0.5-1h, the ISO whiteness ~~can~~ should reach ~~to~~ $75-86^{\circ}$. The pulp is sent into the conventional screening process for fine screening. The refined pulp is sent into the ~~centrifugal-cleaning process before it is~~ condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield is 75%.

~~Comparing~~ Compared with current technology ~~prior arts~~, the method of the

invention has the following advantages as follows: It ~~it~~ is practically a preparation process of pulp which involves a method with close-loop is fully closed, zero discharging, self-cycling, ~~non-acid~~ no acid needed, ~~non-alkali~~ no alkali needed, ~~non-chlorine~~ no chlorine needed, ~~non-anthraquinone~~ no anthraquinone needed, ~~non-cooking~~ no cooking needed, non-bleaching, ~~non-draining~~ and ~~non-pollution~~ no pollution. The method has ~~characters~~ characteristics of saving energy, saving water and being a clean pulping method, and it solves pollution of papermaking completely, ~~utilizes~~ facilitates the re-use of resource of agriculture and forest resources, and protects the biological environment environment. In accordance with the present invention, the fully closed, self-cycling, zero discharge discharging refers to: All raw materials are pretreated and then sent to the oxidizing dipping reaction system; all water in the process from the pretreatment of ~~raw materials till the delivery of it to the oxidation reactor~~ is divided into two parts to ~~accomplish the self-cycling~~ be self-cycled in the process:- One one part is the water from the process of materials ~~cleaning pretreatment~~. It is purified by centrifugal cleaning and beating, during which and the solid sediments ~~in it~~ are taken away. The and the pulps are sent to the ~~common~~ conventional beating process:- Water water generated in the process is cycled into the purification pool. A 0.1%-0.15% ozonizer (O₃ generator) is ~~and a~~ active carbon nutsch filter are installed in the purification pool to decolor the water. The water contains minor oxygen free radical radicals and it is pumped into the cycling water system. The other part is the water from the oxidizing following process:- After the pulp is cleaned with centrifugal cleaner and then is concentrated with a common after conventional decker, the ~~pulp~~ it is sent to the pulp tank for and then to papermaking plant. The ~~produced~~ produced water is filtrated and placed in the water-purifying tank for self-cycling. The purified water is pumped into materials

cleaning system, ~~oxygen-oxidizing-dipping~~ system, oxygen grinding system and ~~filtrating-system-for-recycling-use~~ screening system for being recycled within the company. No ~~any~~-gas or black liquor is drained in the process. The ~~mixed-solid~~ residue ~~discharged~~ only ~~occupied~~ occupies 12%-22% of the materials by weight. This process is pollution-free and the residue can be sent to bio-oxidation treatment tank for other uses.

Caption-Description of the drawings:

Figure.1 is the ~~The flow sheet-chart~~ of this invention that is a fully-~~closed,~~ self-cycling, zero discharge discharging and clean pulping process by oxidation is illustrated in Figure 1.

Detailed description of this invention

EXAMPLE

Undermentioned examples are ~~farther~~-further description of the invention. These examples are only used to describe the invention, not ~~used~~-to limit the ~~conceptual-scope~~ framework of the invention.

EXAMPLE I

100kg full cotton stalks ~~are-were~~ removed of legumen, ~~and~~ calyces by a crushing engine and cut into pieces with a length of 5cm and thick-a thickness of 1.5cm with a yield of. Finally ~~materials with forming-rate 98%-are~~ obtained. Above materials ~~a~~ were broken into plush by a roller-type and-crushing engine, ~~had removed~~-dust and medulla removed by wind power, ~~removed~~ impurity removed by screening, washed by with circular-cycling water before the materials is were transported to the oxidation reactor (an auto agitator is installed in the reactor) by a screw feeder. The reaction conditions ~~a~~ were at 60°C, pH_2.5, a rotating speed of 60 ~~r/s~~ r/min, and with the addition of MgCO₃ 0.02 kg, and

~~bimethyl-bioxirane~~ dimethyl-dioxirane (DMD) 0.01 kg ~~is added~~. After 0.5h, a H_2O_2 solution with weight percentage concentration 0.2 ~~is~~ was added. Then the rotating speed ~~was becomes~~ increased to 80 ~~r/s~~ r/min and temperature ~~is to~~ 80°C. After 1h, impregnating softness ~~number~~ rate of the materials in the reactor ~~is was~~ 98%. The materials ~~change~~ changed from deep yellow to pale white and ~~accord met~~ with ISO whiteness 48-52° (hereinafter it is called whiteness or ISO whiteness for ~~short~~ convenience). Above materials ~~are were~~ washed repeatedly and dewatered to concentrate, ~~and giving a~~ weight percentage concentration of the water ~~is of~~ 30%. A H_2O_2 solution ~~is was~~ added ~~in into~~ the material washed, and the weight percentage concentration of H_2O_2 in the material ~~is was~~ 0.2. The material ~~is was~~ fed to a refiner ~~continuously and equally~~ homogeneously to be ~~grinded ground~~. The rotating speed of refiner disc ~~is was~~ 600-1200 ~~r/s~~ r/min and the gap between the disks ~~is was~~ 0.2-0.15mm. Slag sifted could ~~slag grinding can be grinded ground~~ and screened repeatedly ~~after screening~~. After being ~~In disposal process of~~ transferred into the cleaner, an edible citric acid aqueous solution with a weight percentage concentration of 0.12 and hydroxylamine with a weight percentage concentration of 0.01 ~~are were~~ added. According to routine beating process, the pulp ~~is was~~ beaten, thereby obtaining an original material ~~that pulp with a~~ yield is 76% and an ISO whiteness is of 52-65°. The process described above can be applied in ~~the~~ village and township enterprises in the area with abundant raw materials. ~~And the~~ The coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

EXAMPLE II

~~In accordance with EXAMPLE I,~~ 100kg raw materials from EXAMPLE I ~~are were~~ fed to the refiner ~~continuously and equally~~ homogeneously and continuously by a screw feeder. In the first refining process H_2O_2 (weight

percentage concentration ~~is~~ was 1.5) prepared in advance ~~are~~ were added to the pulp in a ratio of 1:0.12 (according to weight ratio) and mixed with pulp in the refiner at 60°C, pH3.8 and 12-15% consistency. The rotating speed of refiner ~~is~~ was 1300 ~~r/s~~ r/min and the gap between the disks ~~is~~ was 0.15-0.1mm. The pulp whiteness ~~can be~~ was 6065-75°. In the secondary refining process O₃ (concentration ~~is~~ was 10umol/L) ~~is~~ was added and mixed with pulp at 80°C, pH 3.8, 12-15% pulp consistency and pressure 0.4Mpa. The rotating speed of refiner disc ~~is~~ was 1300 ~~r/s~~ r/min and the gap between the disks ~~is~~ was 0.1mm. After 0.5-1h, the ISO whiteness ~~can~~ should reach ~~to~~ 75-86°C. The pulp ~~is~~ was sent into the conventional screening process for fine screening. The refined pulp ~~is~~ was sent into the ~~centrifugal~~ cleaning process, ~~before it is~~ condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield ~~is~~ was 75%.

EXAMPLE III

Original materials ~~are~~ pulps were obtained by the procedure as conducted for in example I, except that MgSO₄ substitutes substituted for MgCO₃ at the same dosage amount.

EXAMPLE IV

The same procedure as conducted for in example II was repeated, except that superoxide anion radicals ($\text{O}_2^{\cdot -}/\text{HOO} \cdot$ $\text{O}_2^{\cdot -}/\text{HOO} \cdot$) whose concentration is was 10umol/L substitutes substituted for O₃ whose concentration ~~is~~ was 10umol/L.

EXAMPLE V

100kg poplar pieces ~~are~~ were broken into plush by a roller-type and crushing

engine, ~~had removed~~ dust and impurity ~~removed~~ by wind power, washed by ~~circular-cycling~~ water before the materials ~~are-were~~ transported to the oxidation reactor (~~an~~ auto agitator ~~is-was~~ installed in the reactor) by ~~a~~ screw feeder. The reaction conditions ~~are-were~~ at -60°C , pH 2.5, rotating speed of 60 ~~r/s~~ r/min and MgSO_4 0.015kg and ~~bimethyl-bioxirane~~ dimethyl dioxirane (DMD) 0.01 kg ~~are~~ were added. After 0.5h, H_2O_2 solution ~~whose~~ with a weight percentage concentration ~~is-of~~ 0.2 ~~is-was~~ added. Then the rotating speed ~~becomes~~ became 80 ~~r/s~~ r/min and temperature ~~is-was~~ 100°C . After 1h, impregnating ~~expanding~~ softness ~~number-rate~~ of the materials in the reactor ~~is-was~~ 98%. The color of the materials ~~change~~ changed from deep yellow to pale white and ISO whiteness ~~is~~ was $48-52^{\circ}$. Above materials ~~is-were~~ washed repeatedly and dewatered to concentrate, and weight percentage concentration of ~~the-water~~ ~~is-was~~ 30%. O_2 and H_2O_2 solution ~~is-was~~ added in dropwise into the material, and weight percentage concentration of O_2 and H_2O_2 in the materials ~~is-was~~ 0.25. The materials ~~are-were~~ fed to ~~a refiner continuously and equally~~ homogeneously by a screw feeder so as to be grinded ground. The rotating speed of refiner disc ~~is~~ was 600-1200 ~~r/s~~ r/min and the gap between the disks ~~is-was~~ 0.2-0.15mm. Slag ~~grinding-sifted~~ ~~can-could~~ be grinded ground and screened repeatedly ~~after screening~~. After being treated in the ~~In cleaner-disposal process~~, ~~an~~ edible citric acid aqueous solution whose weight percentage concentration ~~is-was~~ 0.12 and N, N-dialkyl hydroxylamine whose weight percentage concentration ~~is-was~~ 0.01 ~~are~~ were added. According to routine beating process, the pulp ~~is-was~~ beaten, thereby obtaining an original pulp material whose with a yield of ~~is~~ 76% and ISO whiteness ~~of~~ is $52-65^{\circ}$.

EXAMPLE VI

100kg ~~poplar pieces~~ are original pulp prepared in example V ~~was~~ fed to a

refiner ~~continuously and equally~~ continuously and homogeneously by a screw feeder. In the first refining process, compound oxygen ~~made consisting of~~ H₂O₂ (weight percentage concentration ~~is was~~ 1.5) and O₂ (weight percentage concentration ~~is was~~ 0.1) prepared in advance ~~are was~~ added to the pulp in a ratio of 1:0.15 (according to the weight ratio) and mixed with pulp in the refiner at 60°C, pH3.8 and 12-15% consistency. The rotating speed of refiner ~~is was~~ 1300 r/sr/min and the gap between the disks ~~is was~~ 0.15-0.1mm. The pulp whiteness ~~can be was~~ 60 65-75°. In the ~~secondary~~ second refining process superoxide anion radicals ($\text{O}_2^{\cdot-}/\text{HOO}^{\cdot-}$ ~~$\text{O}_2^{\cdot-}/\text{HOO}^{\cdot-}$~~) (concentration ~~is~~ 10umol/L) ~~is was~~ added dropwise and mixed with the pulp at 80°C pH3.8, 12-15 wt% pulp consistency and 0.4Mpa. The rotating speed of refiner disc ~~is was~~ 1300 r/s r/min and the gap ~~is was~~ 0.1mm. After 0.5-1h, the ISO whiteness ~~can should reach to~~ 75-86°. The pulp ~~is was~~ sent into the conventional screening process for fine screening. The refined pulp ~~is was~~ sent into the ~~centrifugal~~ cleaning process, ~~before it is~~ condensed with a decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and the pulp yield is was 75%.

EXAMPLE VII

Original ~~materials pulp are~~ was obtained by the same procedure as conducted ~~for in~~ example V, except that ~~ETPA substitute~~ DTPA substituted for DMD at the same dosage amount.

EXAMPLE VIII

The same procedure as conducted ~~for in~~ example VI was carried out, except that singlet oxygen (¹O₂) whose concentration ~~is was~~ 10umol/L and O₃ whose concentration ~~is was~~ 10umol/L ~~substitute~~ substituted for superoxide anion

radicals ($\text{O}_2^{\cdot-}/\text{HOO} \cdot$ $\text{O}_2^{\cdot-}/\text{HOO} \cdot$) whose concentration is was 10umol/L.

In accordance with the present invention, there is provided a ~~non-cooking~~ cooking-free, ~~non-conventional~~ no bleaching needed, fully closed, self-cycling and active oxygen mixed refining process. The ~~unexpected~~ undesirable chemicals such as ~~strong-chlorine~~ chlorine, strong acid, strong alkaline are not employed. According to the market demands, the ~~enterprise~~ enterprises can produce various types of ~~middle or high quality pulp~~ pulps of middle or high quality.

The test results of the clean pulp produced by the oxidizing-pulping process:

Pilot ~~product~~ products, namely pulp pulps of full cotton stalk, mulberry tree, poplar and the full cotton stalk screen fine pulp, ~~was~~ were tested by Tianjin Science and Technology University. The results are shown in the testing report in detail (table 5). It is indicated that ~~bio-oxidation~~ the oxidizing pulping technology can be applied to both wood and non-wood materials, and for example, full cotton stalk, ~~the an agriculture residue waste~~, can be utilized as raw materials for pulping.

~~Testing~~ A comparison between the testing report produced by Tianjin Science and Technology University on Nov 12, 2003 and national sulfite-bleach sulfite-bleaching pulping contrast table are produced by Tianjin Science and Technology University at Nov 12, 2003 is listed in . Please refer to table 3.

Table 3 ~~property~~ Property comparison of bio-oxidation pulp and conventional GMP

Index	GB Standard Of BSP	Upland- Cotton <u>Stalk</u>	Upland- Cotton <u>Stalk</u>	Mulberry Pre-Screened	Poplar Pre-Screened
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		Pre-Screened Pulp	Screened Pulp	Pulp	Pulp
Fiber length(mm)	0. 50	0. 51	0. 65	0. 47	0. 55
Degree of beating (°SR)	45	59	51. 5	58	62
Basis weight (g/ m ²)	58. 2	58. 2	60. 0	59. 0	57. 5
density (g/cm ³)	3. 3	0. 33	0. 32	0. 33	0. 32
Breaking length(Km)	3. 2	3. 81	3. 44	3. 44	3. 07
Tear index (mNm ² /g)	2. 8	2. 9	3. 4	2. 9	2. 5
Burst index (KPam ² /g)	1. 5	1. 9	1. 5	1. 7	1. 4
Brightness (%ISO)	82. 0	68. 69	71. 58	70. 87	75. 17
Opacity (%)	88. 1	95. 91	93. 91	96. 05	94. 07